

Isolation and Concentration of Organic
Substances from Water: An Evaluation of
Supercritical Fluid Extraction

Little (Arthur D.), Inc., Cambridge, MA

Prepared for

Health Effects Research Lab.
Research Triangle Park, NC

Nov 84

EPA-600/1-84-028
November 1984

PB85-138899

ISOLATION AND CONCENTRATION OF ORGANIC
SUBSTANCES FROM WATER
--An Evaluation of Supercritical Fluid Extraction

by

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Contract #68-03-3001

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TECHNICAL REPORT DATA		
(Please read Instructions on the reverse before completing)		
1. REPORT NO. EPA-600/1-84-028	2.	3. RECIPIENT'S ACCESSION NO. P80 5 13889 9
4. TITLE AND SUBTITLE Isolation and Concentration of Organic Substances From Water--An Evaluation of Supercritical Fluid Extraction	5. REPORT DATE November 1984	
	6. PERFORMING ORGANIZATION CODE	
7. AUTHOR(S) Daniel J. Ehntholt, Christopher P. Eppig and Kathleen E. Thron	8. PERFORMING ORGANIZATION REPORT NO.	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Arthur D. Little, Inc. Acorn Park Cambridge, Massachusetts 02140	10. PROGRAM ELEMENT NO. CBMC1A	
	11. CONTRACT/GRANT NO. 68-03-3001	
12. SPONSORING AGENCY NAME AND ADDRESS Health Effects Research Laboratory Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, North Carolina 27711	13. TYPE OF REPORT AND PERIOD COVERED Project Report/Summary	
	14. SPONSORING AGENCY CODE EPA-600/11	
15. SUPPLEMENTARY NOTES P.O. H.P. Ringhand, CSSB, TMD, HERL (CI).		
16. ABSTRACT This study describes the use of supercritical fluid carbon dioxide (SCF CO ₂), as an extraction solvent, for the isolation and concentration of twenty-three specified organic solutes in water at trace levels. This type of direct extraction using a non-toxic, non-hazardous solvent such as carbon dioxide represents a new concept for the isolation and concentration of organic compounds from water. The ability of SCF CO ₂ system to extract and subsequently trap model solutes, with widely varying chemical and physical properties, was generally found to be lacking. Only four of the model solutes (2,4-dichlorophenol, isophorone, phenanthrene and stearic acid) demonstrated recovery values of greater than 40 percent. The low recoveries were to an inefficient trap system, adsorption, and the inability of supercritical fluid CO ₂ to extract highly water soluble or alkaline solutes.		
17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
18. DISTRIBUTION STATEMENT Release to Public	19. SECURITY CLASS (This Report) Unclassified	21. NO. OF PAGES 68
	20. SECURITY CLASS (This page) Unclassified	22. PRICE

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FOREWORD

The many benefits of our modern, developing, industrial society are accompanied by certain hazards. Careful assessment of the relative risk of existing and new man-made environmental hazards is necessary for the establishment of sound regulatory policy. These regulations serve to enhance the quality of our environment in order to promote the public health and welfare and the productive capacity of our Nation's population.

The complexities of environmental problems originate in the deep interdependent relationships between the various physical and biological segments of man's natural and social world. Solutions to these environmental problems require an integrated program of research and development using input from a number of disciplines. The Health Effects Research Laboratory, Research Triangle Park, NC and Cincinnati, OH, conducts a coordinated environmental health research program in toxicology, epidemiology, and clinical studies using human volunteer subjects. Wide ranges of pollutants known or suspected to cause health problems are studied. The research focuses on air pollutants, water pollutants, toxic substances, hazardous wastes, pesticides, and non-ionizing radiation. The laboratory participates in the development and revision of air and water quality criteria and health assessment documents on pollutants for which regulatory actions are being considered. Direct support to the regulatory function of the Agency is provided in the form of expert testimony and preparation of affidavits as well as expert advice to the Administrator to assure the adequacy of environmental regulatory decisions involving the protection of the health and welfare of all U.S. inhabitants.

This report presents the results obtained during the development and evaluation of supercritical fluid extraction for the isolation and concentration of trace organic substances from water. Methods for the trace enrichment of organic contaminants in water are essential in determining potential health problems associated with waterborne organic contaminants since existing in vivo and in vitro biological test systems lack the necessary sensitivity for testing water samples.

F. Gordon Hueter, Ph.D.
Director
Health Effects Research Laboratory

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ABSTRACT

This study describes the use of supercritical fluid carbon dioxide (SCF CO₂), as an extraction solvent, for the isolation and concentration of twenty-three specified organic solutes in water at trace levels. This type of direct extraction using a non-toxic, non-hazardous solvent such as carbon dioxide represents a new concept for the isolation and concentration of organic compounds from water. Most of the recovery studies performed on the model compounds were conducted on 400 mL aqueous samples in a stainless steel extractor operated at 2,500 psi and 45°C.

The ability of SCF CO₂ system to extract and subsequently trap model solutes, with widely varying chemical and physical properties, was generally found to be lacking. Only four of the model solutes (2,4-dichlorophenol, isophorone, phenanthrene and stearic acid) demonstrated recovery values of greater than 40 percent. The low recoveries were attributed to the inability of SCF CO₂ to extract highly water soluble or alkaline solutes such as glucose, glycine, trimesic acid, quinaldic acid, humic acid, caffeine, 5-chlorouracil and quinoline. Mass balance studies also indicated losses as a result of an ineffective trap system for volatiles (chloroform, furfural and methylisobutyl ketone) and possibly adsorption to the extraction system for hydrophobic compounds (biphenyl, 1-chlorododecane, and 2,2',5,5'-tetrachlorobiphenyl). The model solutes were monitored using GC/FID, HPLC/UV/fluorescence, and GC/MS procedures developed specifically for this project.

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FOR TABLES
AND ILLUSTRATIONS

CONTENTS

Foreword	iii
Abstract	iv
Figures.	vi
Tables	vii
Acknowledgement.	viii
1. Introduction.	1
2. Conclusions	4
3. Recommendations	6
4. Materials and Methods	7
General Approach	7
Materials Quality Control.	7
Small Scale Extractor.	9
Ten Liter Extractor.	11
5. Experimental Procedures	12
6. Results and Discussions	16
General.	16
Small Scale Extractions of Organic Compound Groups	16
Trapping Experiments	25
Small Scale Extractions of Inorganic Species	33
Chlorine Residual Extraction	36
Ten Liter Extraction of Twenty-Three Organic Species	36
References	43
Appendices	
A. Sample Preparation and Analysis Procedures.	45
B. Typical Sample Preparation and Analytical Finish QA/AC Data	56

FIGURES

<u>Number</u>		<u>Page</u>
1	Supercritical Fluid Extraction Apparatus	10

TABLES

<u>Number</u>		<u>Page</u>
1	Model Compound Purity	8
2	Organic Substances Selected for Study	13
3	Analytical Methods for Compounds Under Study	15
4	Group 1 Extractions	17
5	Group 2 Extractions	18
6	Group 3 Extractions	20
7	Group 4 Extractions	21
8	Extraction of Acid Group	22
9	Extraction of Phenanthrene	23
10	Extraction of 5-Chlorouracil	24
11	Extraction Conditions for 2.0 ppm Humic Acid Solutions	26
12	Vapor Pressure of 2,4-Dichlorophenol	29
13	Trapping Experiments Data	31
14	Results of Trapping Experiment 4	34
15	Trapping Experiment 5 Using a Solid Sorbent Tube	35
16	Extraction of Aqueous Salt Solutions	37
17	Extraction Conditions for Chlorine Residual Study	38
18	Spiking Procedure for Runs 1, 3 and 4	39
19	Summary of Ten Liter Extractions	41
20	Total Organic Carbon Content of Selected Ten Liter Run Samples.	42

ACKNOWLEDGEMENT

The suggestions, support, and encouragement of Dr. Paul Ringhand of the Environmental Protection Agency's Health Effects Research Laboratory are gratefully acknowledged. In addition, the efforts of R. Bruni, R. Cruz-Alvarez, L. Guilmette, M. Randel, A. Tucci, D. Wilson and C. Wong were essential to the completion of this work.

SECTION 1

INTRODUCTION

One approach to understanding and evaluating the possible toxicological effects of the consumption of organic substances found in drinking waters is through the use of biological tests. Many of these tests using experimental animals or organisms require concentration levels of the organic compounds that are significantly higher than normally found in drinking waters. Although hundreds of organic compounds have been identified and quantified in samples of natural waters, much of the organic matter present cannot readily be characterized using currently available analytical protocols. Without such prior qualitative and quantitative identification of the substances, they cannot be purchased or synthesized for use in preparation of the concentrated solutions required for health-effects testing.

Direct concentration of the organic materials from aqueous samples offers an attractive alternative which circumvents the analytical problems associated with the identification and quantification of wide varieties of species present at trace levels. A number of techniques have been studied for their utility in effecting such concentrations. These have included the use of reverse osmosis, solid sorbents, and liquid/liquid extractions (1). Serious problems may, however, be encountered in the use of concentrated solutions prepared by these methods due to the inadvertent contamination of the sample. For example, membrane techniques may introduce impurities from the membrane, and may not selectively isolate organic substances from inorganic species. Collection of organics on sorbents followed by recovery with organic solvents also poses a number of problems. Concerns have been expressed over the large blank contributions of resins, possible interactions of the organic substances concentrated with the solvents (or impurities present in them) used for desorption, and the presence of traces of solvent in the prepared sample. The liquid/liquid extraction techniques utilizing organic solvents yield concentrations of organic substances in media which may be undesirable for animal feeding studies. For example, immediate concern can be expressed about the use of benzene or the halogenated one- and two-carbon compounds which are known or suspect carcinogens if long-term biological tests are to be performed.

The present study has focused on the use of supercritical fluid carbon dioxide for the concentration and/or isolation of specified organic compounds present in waters at trace levels. This type of direct extraction using a non-toxic, non-hazardous solvent such as carbon dioxide represents an entirely new concept for extracting trace levels of organic compounds from water.

Solubility phenomena in supercritical fluids were first reported by Hanney and Hogarth in 1879 (2). They found that inorganic salts such as cobalt chloride and potassium iodide could be dissolved in supercritical ethanol and ether, and they found, furthermore, that the solubility level increased with increasing pressure.

In the early 1900's Bucher (3) studied the solubilities of a number of organic materials in supercritical carbon dioxide. His results showed that the concentration of organic species such as naphthalene, phenanthrene, phenols, and other aromatics dissolved in supercritical carbon dioxide was many times that which would be expected from the normal increase in vapor pressure due to external pressure. Other supercritical fluid solubility studies of the early 1900 period were directed to similar considerations of solution thermodynamics, multi-phase equilibria, etc. Booth and Bidwell (4) present an excellent review of the developments during this period.

During the 1940's, a large amount of solubility data was obtained by Francis (5,6) who carried out measurements on literally hundreds of binary and ternary systems with liquid carbon dioxide just below its critical point. Francis found that liquid carbon dioxide is also an excellent solvent for organic materials and that many of the compounds studied were completely miscible.

In 1955 Todd and Elgin (7) reported on phase equilibrium studies with supercritical ethylene and a number of low vapor pressure organic materials such as fatty acids and high molecular weight alcohols, and like the investigators before them, they found solubility levels of the organic species to be orders of magnitude higher than those predicted by vapor pressure considerations. Their findings led them to write, "The magnitude...of solubility... is sufficient to consider the gas as an extracting medium, that is, fluid liquid or fluid solid extraction, analogous to liquid/liquid extraction and leaching...thus, compression of a gas over mixture of compounds could selectively dissolve one compound, permitting it to be removed from the mixture." This was the first published reference to potential extraction process applications of solubility in supercritical fluids.

A few years later Elgin and Weinstock (8) reported that a number of organic-water mixtures could be separated into organic-rich and water-rich phases using supercritical ethylene, and they presented process concepts for separating such mixtures. Since Todd and Elgin's paper in 1955, descriptions of a number of process applications of supercritical fluid solubility have appeared in the literature. Much of the effort reported has been directed to the extraction of edible (9) and essential (10) oils and other food and beverage products such as spices (11), coffee (12) and hops (13) using either supercritical or near-critical liquid carbon dioxide. The attributes of carbon dioxide, such as its low cost and absence of safety hazards and toxicity problems, were ideally suited for food applications. In the mid- and late-1960s some development activity was directed towards supercritical fluids chromatography (14) and to extractions of fuels, viz., supercritical fluid extraction of coal (15), petroleum (16) and lignite (17).

Starting in about 1975, development efforts at a number of industrial and academic laboratories increased markedly in both the United States and Europe. The resurgent research activity was motivated by a number of factors, viz.:

Increased scrutiny of certain industrial solvents because of associated health and safety problems,

Increasing costs of traditional but energy-intensive separation processes such as distillation and evaporation,

Increasingly stringent pollution control legislation which increased costs of traditional extraction processes, and

Identification of certain key areas where supercritical fluid processing could be technically, as well as economically, superior to traditional separation processes.

Supercritical fluid separation processes operate at pressures ranging from 1,000 to 4,000 psi, pressures which might be considered high, especially in the foods and essential oils industries. However, because of the above factors, supercritical fluid extraction has become economically attractive irrespective of the pressure requirements. Efforts to date have resulted in the development of several supercritical fluid processes in use throughout the world. Several large pilot plants for coal (18), coal ash (19), and asphalt (20) separation are in operation in the U.S., U.K., and U.S.S.R. Two commercial plants came on stream in 1979 for the extraction of beverage products, one in operation in Germany and the other in Australia, the former for coffee decaffeination (21) and the latter for hops extraction (22). Theoretical and practical efforts leading to several of these developments were summarized at a recent symposium devoted to "Extraction With Supercritical Gases" (21).

These efforts and others suggested there might be process advantages for using supercritical fluid carbon dioxide to extract low concentrations of organics from water. The U.S. Environmental Protection Agency therefore sponsored the work described herein which was designed to evaluate such a process; the work was initiated in late 1980.

SECTION 2

CONCLUSIONS

This study demonstrated the utility of supercritical fluid carbon dioxide for the isolation and concentration of certain types of organic compounds present in water at low concentration levels. In general, compounds which are volatile and/or not highly soluble in water can readily be extracted under the operating conditions used. Those compounds which exhibit greater solubility in water (e.g., trimesic acid and 5-chlorouracil) do not show evidence of extraction; in addition, those materials which tend to precipitate (humic acid) or form more soluble species (caffeine) under acid conditions were not extracted.

An extraction conducted on an aqueous solution containing a two part-per-million chlorine residual did not indicate the generation of any new species in the extract. All of the tests in this program were conducted on aqueous solutions containing NaHCO_3 , CaSO_4 , and CaCl_2 added at concentration levels typical of drinking water.⁴ Experiments were also conducted to determine whether or not these inorganic materials or PbNO_3 (added to several solutions as a surrogate for possible toxic metal concentration) were extracted. Results indicated that the inorganics were not isolated or concentrated.

The extraction conditions used in the study were determined based on approximately seventy percent extraction of Group 4 phenolic compounds in early runs. Additional treatment with supercritical fluid carbon dioxide would increase the extraction efficiency of the process, but might present additional trapping (recovery) problems.

The initial focus of analytical efforts in the program was the quantification of compounds in the aqueous feedstock and raffinate. During the program, it became evident that trapping procedures were critical, due primarily to the small absolute quantities of compound being studied in small scale runs. A series of trapping/recovery experiments conducted during the program suggest that improvements in recovery of organics are possible by adopting modified trapping procedures and altering the techniques used for removal of the organics from the traps for subsequent analysis.

Although the aqueous extraction sampling and analysis procedures were well developed for the study, the trapping and trap rinse procedures were varied on changing from small scale extractions (0.4 liter) to 10 liter extractions. The results obtained for trap recoveries are not therefore

directly comparable, although solution analysis results are comparable. Some trap recovery variations may be due to the operation of the extractor at slightly different rates from experiment to experiment, and the possible loss of extracted organic material through inefficient trapping and/or inefficient rinsing of the trap prior to analysis.

The overall conclusion from this study was that the supercritical fluid carbon dioxide extraction of drinking water represents an alternative path for isolating organic compounds which are not highly soluble in water. It can be used in lieu of organic solvents or membrane techniques when those materials pose interference problems in subsequent tests.

SECTION 3

RECOMMENDATIONS

Since the concept should be adaptable to large scale extraction of certain types of organic compounds from water, further study of the supercritical fluid extraction concept is recommended, focusing on issues which have not been completely examined. Specifically, the efficiencies of alternative trapping systems should be defined. For example, complete trapping of all effluent carbon dioxide in a vessel from which fractional distillation of CO_2 can take place will likely yield higher recoveries of organics. In addition, the use of "closed systems" in which the effluent CO_2 stream is recycled through the aqueous stream after removal of some portion of the dissolved organic compounds may permit more efficient collection of those organics. If these studies are conducted on a small scale, particular attention should be paid to irreversible adsorption to the traps and inefficient removal of the organics from the effluent CO_2 stream as likely causes of low organic compound recovery.

SECTION 4

MATERIALS AND METHODS

GENERAL APPROACH

Twenty-three organic substances were selected as representative of classes of compounds usually encountered in drinking waters. In addition, calcium and sodium salts were added to the aqueous samples to simulate inorganic salt concentrations found in Cincinnati drinking water. Lead nitrate was also studied to determine whether supercritical fluid carbon dioxide might extract and/or concentrate metal salts.

In order to facilitate sample preparation steps and subsequent analyses, initial supercritical fluid carbon dioxide extraction studies were conducted using small groups of similar compounds. These studies utilized four hundred milliliter sample volumes. Final ten liter extractions were run with aqueous samples containing all twenty-three organic substances as well as calcium and sodium salts present at the levels specified for this effort (as further described in the following Section 5 of this report).

MATERIALS QUALITY CONTROL

Standard documentation and quality control procedures were followed throughout this program. Thus, as analytical standards were purchased, the vendor name, catalog number, lot number, quantity, date of receipt, purity, etc., were recorded in laboratory notebooks together with the molecular formula, structure, boiling point, melting point, and any appropriate handling procedures. Each lot of purchased analytical standards was analyzed by differential scanning calorimetry and/or fourier transform infrared spectroscopy, as appropriate. Similarly, derivatives of standards were isolated and melting points compared to literature values.

Liquids used in the program included only distilled, deionized water (Milli-Q system), and HPLC grade distilled-in-glass solvents (Fisher-HPLC or Burdick and Jackson). The carbon dioxide was supplied by Cardox (99.5% purity, balance N₂ and O₂, hydrocarbon content determined by FID 5 vol. ppm as propane). Derivatizing reagents were obtained from Aldrich Chemicals (dinitrophenylhydrazine) and Pierce Chemicals (N-trimethylsilylimidazole and "STOX", Oxime Internal Standard Reagent).

Table 1 lists the suppliers and grade of purity of each of the twenty-three organic compounds studied in this program. The inorganic salts used

TABLE 1. MODEL COMPOUND PURITY

<u>Compound</u>	<u>Supplier</u>	<u>Purity or Grade</u>
Anthraquinone	Fisher	98+%
Biphenyl	RFR Corp.	99%
Bis(2-ethylhexyl)phthalate	Chem. Service	99+%
Caffeine	Aldrich	Reagent
1-Chlorododecane	Eastman	Reagent
Chloroform	Fisher	Certified ACS
5-Chlorouracil	Sigma	Reagent
Crotonaldehyde	Kodak	95+%
2,6-Di-t-butyl-4-methylphenol	Koppers	99+%
2,4-Dichlorobiphenyl	Analabs	99%
2,4-Dichlorophenol	Aldrich	99%
Furfural	Aldrich	99%
Glucose	Aldrich	Reagent
Glycine	Aldrich	98%
Humic Acid	EPA	--
Isophorone	Aldrich	98%
Methyl Isobutyl Ketone	Fisher	Certified ACS
Phenanthrene	Aldrich	98+%
Quinaldic Acid	Aldrich	99%
Quinoline	Aldrich	96%
Stearic Acid	MCB	99.5+%
2,2',5,5'-Tetrachlorobiphenyl	RFR Corp.	99%
Trimesic Acid	Aldrich	97%

were purchased from J.T. Baker Company. In general, all reagents and chemicals were purchased in the highest purity available.

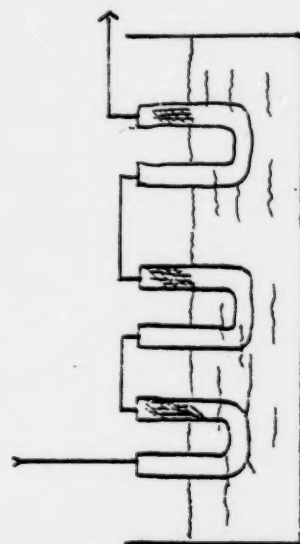
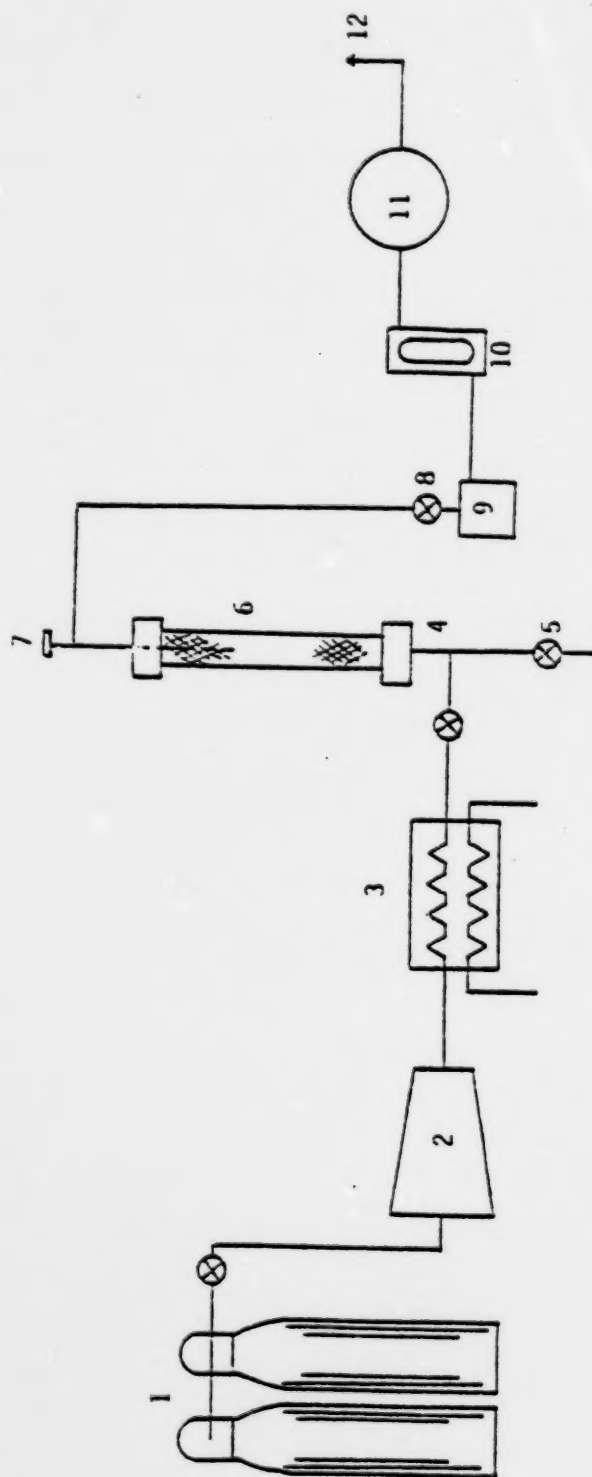
SMALL SCALE EXTRACTOR

Most of the extraction studies carried out under this contract were conducted on 400 milliliter volume aqueous samples in a stainless steel extractor (extractor volume was approximately 600 milliliters) operated at about 2,500 psi (i.e., 173 bar) and 45°C. Supercritical conditions are achieved for carbon dioxide at pressures >1,070 psi (i.e., 73.8 bar) and temperatures >31.1°C. In our tests, approximately 300 standard liters of CO₂ were passed through the aqueous solutions into the trap. The trapping system usually consisted of a set of three sequential glass U-tubes maintained at -76°C by a dry ice-acetone bath. Operation at this temperature precludes clogging by solid CO₂, but may be responsible for loss of some extracted organic materials, as noted later. Other trapping options are discussed in Section 6 of this report.

The experimental apparatus used to perform the supercritical fluid carbon dioxide extractions is shown diagrammatically in Figure 1. Carbon dioxide provided from supply cylinder 1 is compressed by diaphragm compressor 2 and heated to the desired extraction temperature in heat exchanger 3. The pressurized, temperature-adjusted carbon dioxide feed flows through the high pressure fluid inlet line 4 to vessel 6 which contains the aqueous solution to be extracted. The extraction vessel is wrapped with electrical heating tape to regulate the extraction temperature, which is measured with thermocouple 7.

The supercritical carbon dioxide extract stream is passed from the extractor vessel outlet through pressure reduction valve 8, where the pressure is reduced to atmospheric and the extracted organic substance is precipitated in collection device 9. The atmospheric pressure carbon dioxide then flows from the collection device through a rotameter 10 and dry gas meter 11, which measure CO₂ flow rate and total volume, respectively, to the vent 12.

To enhance the CO₂/aqueous phase interfacial area and facilitate contact by dispersion of the CO₂ as fine bubbles, a plug of silanized glass wool was placed in the bottom of the extraction vessel. After charging the vessel with 400 mL of aqueous feedstock solution, the vessel was slowly pressurized to the extraction pressure and simultaneously heated to the desired temperature. Carbon dioxide was then passed through the aqueous phase at a velocity of slightly more than 10 cm/min (about 10 standard liters/min at 1 atm., 70°F). After a pre-determined amount of carbon dioxide (typically 300 standard liters) flowed through the sample, the system was depressurized and the extracted aqueous raffinate was drained through valve 5 into a collection vessel. The extractor and all lines were of stainless steel construction; the traps for the small scale extractions and containers for feedstock and raffinate were all glass.



Trap 9

FIGURE 1. SUPERCRITICAL FLUID EXTRACTION APPARATUS

TEN LITER EXTRACTOR

An original objective of this effort was the extraction of a five-hundred liter samples at the conclusion of the program. During the course of the project, however, it was decided that a smaller-scale run combined with additional trapping experiments would yield more useful results. A final series of ten liter extractions were therefore carried out on solutions containing all of the organic compounds of interest and the three inorganic compounds specified. The extraction apparatus used in these studies was similar to that described earlier for the small-scale work, but had an internal volume of approximately fifteen liters. The traps used were stainless steel impingers with a volume capacity of approximately 1 liter.

SECTION 5

EXPERIMENTAL PROCEDURES

As noted earlier, 23 organic substances were identified for study during this effort. Those compounds and the concentration levels at which they were investigated in this program are shown in Table 2. All of the aqueous solutions for evaluation were prepared by spiking a small aliquot of the organic compounds dissolved in acetone into a distilled, deionized water sample containing 70 ppm NaHCO_3 , 120 ppm CaSO_4 , and 47 ppm $\text{CaCl}_2 \cdot \text{H}_2\text{O}$.

Special care must be exercised in the study of parts-per-billion concentrations of organics in water to assure minimal losses due to sample degradation, adsorption or absorption to process materials, and other similar losses. These parameters were addressed by dividing the measurement procedures into two parts--sample preparation and analytical finish. Since well defined sample preparation steps were not available from the literature for the quantitative determination of parts-per-billion concentration levels of most of the model organic compounds in water, a considerable amount of effort was placed on the development of appropriate procedures for such measurements. In particular, each method was developed with the intent to have a procedure which could verify the presence of appropriate concentrations of the organics in the feedstock and also monitor their concentrations after extraction by carbon dioxide, i.e., to quantify concentrations of organics in the raffinate which were one-fiftieth of the starting concentration level. For some groups of compounds, this effort involved extensive variation and study of sample preparation steps, however, the goal of developing accurate and reproducible methods for studying the concentration of the model compounds in water was met for most of those compounds.

In order to accurately determine the levels of compounds present in the aqueous solutions before and after CO_2 extraction, a sample preparation step involving concentration of the compounds was necessary for most samples. In the case of Groups 1, 2, 3, 4, and 8, microextraction techniques with organic solvents were used (23). For Group 5 acids, resin concentration was used. Group 6 was concentrated by evaporation; Group 7 (chloroform), Group 9 (5-chlorouracil), and Group 10 (humic acids) samples were analyzed as received. Derivatization was used to enhance the detection limits for three of the groups. The formation of 2,4-dinitrophenyl hydrazone derivatives of the Group 2 aldehydes and ketones permitted their determination by an HPLC method after microextraction. Methyl esters of the Group 5 acids were formed using diazomethane, with subsequent detection by GC/FID. Glucose and glycine

TABLE 2. ORGANIC SUBSTANCES SELECTED FOR STUDY

<u>Group</u>	<u>Compound</u>	<u>Concentration Level ($\mu\text{g/L}$)</u>
1	1-Chlorododecane	5
	2,2',5,5'-Tetrachlorobiphenyl	5
	Biphenyl	50
	Bis(2-ethylhexyl)phthalate	50
	2,4'-Dichlorobiphenyl	50
2	Crotonaldehyde	50
	Furfural	50
	Isophorone	50
	Methyl isobutyl Ketone	50
3	Anthraquinone	50
	Quinoline	50
	Caffeine	50
4	2,4-Dichlorophenol	50
	2,6-Di-t-butyl-4-methylphenol	50
5	Quinaldic acid	50
	Trimesic acid	50
	Stearic acid	50
6	Glucose	50
	Glycine	50
7	Chloroform	50
8	Phenanthrene	1
9	5-Chlorouracil	50
10	Humic acid	2000

(Group 6) were quantified after treatment with a hydroxylamine hydrochloride solution in pyridine, followed by N-trimethyl-silylimidazole. The TMS-glucose-oxime derivative and the glycine-TMS derivative thus formed were analyzed using GC/FID methods.

Analytical finish methods for monitoring the compounds were developed or modified to permit the quantification of all 23 compounds of interest. The compounds were initially studied in small scale extractions by groups as designated in Table 3. This approach assured minimal interferences in the analyses conducted during the initial supercritical fluid carbon dioxide extractions. Table 3 identifies the analytical techniques developed to monitor the concentration levels of the compounds before and after extraction by CO₂. For each experimental run, blank and spiked aqueous samples were carried through the sample preparation and analytical finish steps to assure accurate and reproducible results. Details of the sample preparation steps and analytical finishes, including typical quality control data are included in the Appendix to this report. Analyses of sodium, calcium, and lead content were conducted on selected samples using standard atomic absorption spectroscopy methods for inorganic cations present in drinking waters (24).

All of the techniques developed were amenable to the analysis of the concentrated compounds in collection devices (traps). Since these compounds were expected to be present in neat form in the traps, it was not anticipated that the sample preparation aspect of the analysis would pose any difficulty (i.e., it was assumed that any adsorption to glass walls, etc., which might occur would affect only a proportionately very small portion of the collected sample). As is discussed in the following Section 6 of this report, this did not prove to be the case for many of the compounds studied. In addition, the difficulties inherent in trapping trace quantities of organics in the effluent CO₂ stream were not obvious during the early stages of this program.

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TABLE 3. ANALYTICAL METHODS FOR COMPOUNDS UNDER STUDY

<u>Group</u>	<u>Compound</u>	<u>Analytical Method</u>
1	1-Chlorododecane 2,2',5,5'-Tetrachlorobiphenyl Biphenyl Bis(2-ethylhexyl)phthalate 2,4'-Dichlorobiphenyl	GC/FID GC/FID GC/FID GC/FID GC/FID
2	Crotonaldehyde Furfural Isophorone Methyl isobutyl ketone	2,4-Dinitrophenyl hydra- zone derivatization, then HPLC/UV
3	Anthraquinone Quinoline Caffeine	GC/FID GC/FID GC/FID
4	2,4-Dichlorophenol 2,6-Di-t-butyl-4-methylphenol	Diazomethane derivatization, then GC/FID
5	Quinaldic acid Trimesic acid Stearic acid	TMS/Oxime derivatization then GC/FID
6	Glucose Glycine	TMS/Oxime derivatization then GC/FID
7	Chloroform	GC/FID
8	Phenanthrene	HPLC/UV/Fluorescence
9	5-Chlorouracil	HPLC/UV
10	Humic acid	HPLC/UV

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SECTION 6

RESULTS AND DISCUSSION

GENERAL

As discussed in Section 4 of this report, a series of small scale extractions of various groups of organic compounds were conducted. In all cases, the specified concentrations of NaHCO_3 , CaCl_2 , and CaSO_4 were present in the aqueous samples. Experiments were also conducted on a small scale to study the effects of the extraction technique on inorganic salts and a chlorine residual. In order to obtain a meaningful data set for the final extraction of 10 liter aqueous samples, that series of experiments was conducted in triplicate. Humic acid was added to the solutions in the last series to study its effect on the recovery of organics. Throughout these efforts, "blank" samples were also run in order to determine whether any impurities might be introduced by the procedure. These experiments are described in the following paragraphs.

SMALL SCALE EXTRACTIONS OF ORGANIC COMPOUND GROUPS

Table 4 details the experimental results obtained for the supercritical fluid carbon dioxide extraction of the Group 1 compounds. The compounds investigated, nominal spiking levels, and a number of experiments performed are listed in the first three columns. The mean recoveries for each of the three U-tube traps connected in series are then presented along with the total recoveries obtained from all three traps. The quantity of compound recovered from the raffinate (effluent) solution after CO_2 extraction is contained in the last column. Although four of the five compounds spiked into the aqueous samples could be recovered from the traps, only 20% to 31% of the total mass of each compound could be accounted for when the amounts in the traps and raffinate were summed. Losses may be due to incomplete trapping because of the low, but measureable vapor pressures of these compounds and the large volume of CO_2 passed through the traps. This possibility is further explored in the subsequent discussion on trapping experiments. Table 5 shows recoveries for the Group 2 aldehydes and ketones investigated. Results from the two experiments conducted on the aldehydes and ketones are shown separately to illustrate the care which must be exercised in conducting and evaluating these runs. Both CO_2 extractions were performed under similar conditions, however, in the second run the U-tube traps were contacted with the 2,4-dinitrophenylhydrazine derivatizing solution for longer periods of time. This modification in the analytical procedure permitted higher total mass accountabilities in the second experiment, ranging from 64.9% for isophorone

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TABLE 4. GROUP 1 EXTRACTIONS

Trap Recoveries (%)

Compound	Concentration Level (µg/L)	Number of Experiments	Trap 1, 2, 3			Total Traps			Raffinate		
			Mean Recovery			Mean Recovery			Mean Recovery		
1-Chlorododecane	5	1	0, 0, 0			0			20.7	-	-
2,2',5,5'-Tetra- chlorobiphenyl	5	3	18.7, 0, 0			18.7			12.0	20.8	
Biphenyl	50	1	9.1, 11.0, 3.3			23.4			3.8	-	-
Bis(2-ethylhexyl)- phthalate	50	3	11.3, 0, 0			11.3			15.4	17.5	
2,4'-Dichlorobi- phenyl	50	3	15.7, 4.6, 0			20.3			8.5	10.8	

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TABLE 5. GROUP 2 EXTRACTIONS

Trap Recoveries (%)

Raffinate
Recovery

Total
Traps
Recovery

Trap 1, 2, 3
Recovery

Number of
Experiments

Concentration
Level ($\mu\text{g/L}$)

Compound

Crotonaldehyde

Furfural

Isophorone

Methyl Isobutyl
Ketone

25.1
31.0

1.0
7.8

0.8, 0, 0.2
7.0, 0.8, 0.1

2

50

43.4
22.3

3.8
10.8

3.7, 0, 0.1
8.3, 2.5, 0

2

50

17.8
24.5

1.7
40.4

0, 0, 1.7
39.2, 0.7, 0.5

2

50

7.4
11.4

0
17.3

0, 0, 0
15.6, 1.5, 0.2

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to 28.7% for methyl isobutyl ketone. The recoveries from the raffinate for each of these compounds remained relatively constant, suggesting that the trap recoveries in the first case were artificially low.

Table 6 details the extraction results found for Group 3 compounds anthraquinone, caffeine, and quinoline. It seems likely that the low trap recoveries and high residual concentrations of quinoline and caffeine in the raffinate are due to the low pH of the extracting media (pH ~3) with the resulting poor solubility of these nitrogenous compounds in the CO₂ effluent stream. Anthraquinone was recovered in good yields from the same extractions.

Table 7 presents our data for the similar extraction of Group 4 phenols from aqueous solutions. The o-bromophenol was added as an internal standard when some initial recovery problems were noted for the 2,6-di-t-butyl-4-methylphenol; results for its extraction are also reported here. The three phenols show good recoveries in the traps and overall good mass recoveries. One experiment was conducted under liquid CO₂ extraction conditions (temperature = 30°C and pressure = 1,500 psi) in an attempt to compare the relative efficiencies of the two states of CO₂ for phenol extraction. Unfortunately, the phenols showed evidence of substantial "breakthrough" from the trapping system. The experiment does, however, demonstrate that liquid CO₂ is also a good extractant for phenols present in water at parts-per-billion concentration levels.

Group 5 acids present at the 50 ppb level in aqueous solutions containing the specified inorganic salts were also extracted. The feedstock solution (pH 7.2) and the raffinate (pH 4.5) were analyzed by concentration on XAD-7 resin, elution by methanol, methylation by diazomethane, and finally, measurement of peak areas by GC/FID. Comparison of the peak areas of the raffinate with the peak areas in the original solution indicated a 78% reduction for stearic acid, 15% for quinaldic acid and 9% for trimesic acid. The three traps, including the glass-wool plugs and connecting tubes were also analyzed for acid content. Only stearic acid was detected. The results are summarized in Table 8.

Group 6 compounds glucose and glycine were not tested at the small scale level, since previous work suggested that they would not be soluble in supercritical fluid CO₂. Additionally, chloroform was not tested at this level since it is undoubtedly extractable, but would pose significant trapping problems due to its relatively high vapor pressure.

Group 8 compound phenanthrene was tested in a 1 ppb (µg/L) solution, and showed virtually complete recovery as detailed in Table 9. Group 9 compound 5-chlorouracil, on the other hand, did not exhibit any extraction. Recovery of the compound in the raffinate (at the 50 ppb level) was quantitative, indicating that little, if any was extracted (Table 10).

Several extractions were also conducted on 2.0 milligram/liter humic acid solutions. These were prepared by dissolving a known quantity of humic acid (Fluka, further purified by EPA personnel) in 0.20 M sodium hydroxide followed by dilution with water to a 0.02 M sodium hydroxide solution. Subsequent neutralization to pH 7.0 with 0.100 M HCl and dilution with water containing

TABLE 6. GROUP 3 EXTRACTIONS

Trap Recoveries (%)

Compound	Concentration Level (ug/L)	Number of Experiments	Trap 1,2,3	Total Traps		Raffinate	
				Mean Recovery	Std. Dev.	Mean Recovery	Std. Dev.
Quinoline	50	2	1.7, 1.7, 0	3.4	3.7	46.1	14.3
Caffeine	50	2	0, 0, 0	0	-	81.4	11.4
Anthraquinone	50	2	56.0, 14.3, 14.3	84.6	38.3	21.4	30.2

TABLE 7. GROUP 4 EXTRACTIONS

Compound	Concentration Level (ug/L)	Number of Experiments	Trap Recoveries (%)				Raffinate	
			Trap 1,2,3	Total Traps		Raffinate Mean Recovery	Mean Recovery	Std. Dev.
				Mean	Std. Dev.			
2,4-Dichlorophenol	50	3(SCF CO ₂) 1(Liquid CO ₂)	35.8, 9.6, 0	45.4	15.0	28.0	28.0	14.0
			15.3, 16.8, 8.2	40.3	-	13.4	13.4	-
2,6-Di-t-butyl- 4-methylphenol	50	3(SCF CO ₂) 1(Liquid CO ₂)	26.6, 6.0, 0	32.7	3.0	0	0	-
			8.7, 10.7, 6.6	26.0	-	6.8	6.8	-
o-Bromophenol	50	3(SCF CO ₂) 1(Liquid CO ₂)	24.6, 17.0, 0	41.7	15.6	31.6	31.6	9.6
			10.8, 12.3, 10.8	33.9	-	19.5	19.5	-

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TABLE 8. EXTRACTION OF ACID GROUP

Compound	Concentration Level ($\mu\text{g/L}$)	Number of Experiments	Trap Recoveries (%)		Raffinate (%)
			Trap 1, 2, 3	Total Traps	
Stearic Acid	50	1	25, 2.5, 20	47.5	22
Quinaldic Acid	50	1	0, 0, 0	0	85
Trimesic Acid	50	1	0, 0, 0	0	91

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TABLE 9. EXTRACTION OF PHENANTHRENE

<u>Compound</u>	<u>Concentration Level ($\mu\text{g/L}$)</u>	<u>Number of Experiments</u>	<u>Trap Recoveries (%)</u>		<u>Raffinate (%)</u>
			<u>Trap 1, 2, 3</u>	<u>Total Traps</u>	
Phenanthrene	1	1	58, 36, 3	97	0

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TABLE 10. EXTRACTION OF 5-CHLOROURACIL

<u>Compound</u>	<u>Concentration Level (µg/L)</u>	<u>Number of Experiments</u>	<u>Trap Recoveries (%)</u>		<u>Raffinate (%)</u>
			<u>Trap 1, 2, 3</u>	<u>Total Traps</u>	
5-Chlorouracil	50	1	0, 0, 0	0	96%

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the salts noted earlier gave a 2.0 mg/L humic acid solution for extraction studies. Three supercritical fluid carbon dioxide extractions were carried out on this solution; no humic acid could be detected in the traps.

Table 11 lists extraction conditions tried in these runs. It was observed that although the analyses of feedstock solutions showed the presence of 97.7% to 104.7% of the expected concentration levels of humic acids, analyses of raffinate solutions showed lower humic acid concentrations. The raffinate obtained after the CO₂ extraction indicated that the humic acids were present at 39.4% to 44.9% of the feedstock levels (as measured by HPLC/UV). This suggested that the acidic conditions present in the extractor caused some precipitation and resultant loss of material. Cleaning of the extractor after these experiments indicated that, in fact, a dark organic material had precipitated on the walls of the extractor. In addition, an experiment was conducted on the neat humic material (in the absence of water) to verify that the organic substance was not dissolved or carried over into the trapping system. In that case, approximately five hundred milligrams of humic acid material was treated sequentially with one hundred standard liters of carbon dioxide (2500 psig at 45-50°C) and 50 standard liters (4000 psig at 38-41°C). There was no apparent collection of material in the traps (visually or gravimetrically), and there was only a very slight loss (<5% gravimetric) of the starting mass. That loss may have been due to sample handling procedures. This experiment thus verified the non-extraction of humic materials in the tests noted earlier.

TRAPPING EXPERIMENTS

The system used to collect the organic compounds extracted from the aqueous stream was, in most cases, a series of glass U-tubes held at -76°C. That temperature represented a practical lowest limit to prevent deposition of solid carbon dioxide. During the course of this program, it became evident that, for many compounds, complete mass balances were not being achieved. The trapping system appeared to be a likely source of such losses, since many of the compounds being studied have a finite vapor pressure at -76°C. An effluent CO₂ stream saturated with those compounds, even at -76°C, might, therefore, be responsible for those losses if enough CO₂ was passed through the traps. Other possible sources of compound losses would, of course, included entrainment in the CO₂ stream or adsorption to the trap walls, with inefficient rinsing of the trap before analysis.

By knowing the concentration of the organic in the CO₂ extract, and the vapor pressure of the organic substance at the U-tube trap temperature, it is possible to complete a material balance around the U-tube, and thus determine its theoretical trapping capability. The material balance in the U-tube can be represented by the equation:

$$Fy' - Fy_{vp} = \frac{d \text{ U-tube}}{dt} \quad (1)$$

where F is the molal flow rate of carbon dioxide, moles/unit time,

TABLE 11. EXTRACTION CONDITIONS FOR 2.0 ppm HUMIC ACID SOLUTIONS

Experiment No. 1:	Sample Volume: 400 mL of solution
	Temperature: 45°C ($\pm 3^\circ$)
	Pressure: 2400 psi (± 100)
	CO ₂ Volume: 300 Standard liters
Experiment No. 2:	Sample Volume: 400 mL
	Temperature: 46°C ($\pm 3^\circ$)
	Pressure: 2450 psi (± 50)
	CO ₂ Volume: 340 SL
Experiment No. 3:	Sample Volume: 400 mL
	Temperature: 46°C ($\pm 3^\circ$)
	Pressure: 2200 psi (± 50)
	CO ₂ Volume: 580 SL

y' is the concentration of organic in the carbon dioxide extract phase entering the U-tube, moles/mole CO_2 ,

y_{vp} is the concentration of organic in the carbon dioxide leaving that U-tube, moles/mole CO_2 , and

U-tube is the moles of organic collected in the U-tube.

Equation 1 can be integrated to yield:

$$\int_0^T F y' dt - F y_{vp} T = \text{U-tube} \quad (2)$$

The percent capture (under ideal conditions) of organic being fed to the U-tube is thus:

$$\% \text{ U-tube capture} = \frac{\int_0^T F y' dt - F y_{vp} T}{\int_0^T F y' dt} \times 100 \quad (3)$$

To evaluate expression 3, y' can be obtained from distribution coefficient considerations as:

$$y' = x'_1 K \exp\left[-K \frac{Ft}{W}\right]$$

x'_1 is the initial concentration of organic in solution, moles/mole water,

K is the distribution coefficient $\frac{y'}{x'}$,

F is the molal flow rate of carbon dioxide, moles/unit time, and

W is the initial charge of water, moles.

This expression is substituted into the integral in equation 3 and the integral evaluated:

$$\int_0^T F y' dt = -F x' K \frac{1}{KF/W} \exp\left[-K \frac{FT}{W}\right] \Big|_0^T$$

$$= x'_1 W \left\{ 1 - \exp\left[-K \frac{FT}{W}\right] \right\} \quad (5)$$

Thus, the theoretical U-tube recovery is:

$$\% \text{ U-tube capture} = \left\{ \frac{1 - \exp\left[-K \frac{FT}{W}\right] - \frac{FT}{x'_1 W} y_{vp}}{1 - \exp\left[-K \frac{FT}{W}\right]} \right\} = 100 \quad (6)$$

Using the data from small scale extraction of dichlorophenol as an example, the ideal U-tube recovery can be calculated:

$$1 - \exp\left[-K \frac{FT}{W}\right] = 1 - \exp\left[-(2.58) \frac{(12.61)}{(22.20)}\right] = 0.769$$

$$x'_1 = \frac{54.98 \times 10^{-6} \text{ g DCP} / 163.01 \text{ g DCP/Mole DCP}}{1000 \text{ g H}_2\text{O} / 18.02 \text{ g H}_2\text{O/mole H}_2\text{O}} = 6.078 \times 10^{-9} \frac{\text{moles DCP}}{\text{mole H}_2\text{O}}$$

y_{vp} = vapor pressure DCP at U-tube temperature/total pressure

$$= 2 \times 10^{-6} \text{ mm Hg} / 760 \text{ mm Hg} = 2.63 \times 10^{-9} \quad (*\text{from Table 12})$$

$$\frac{FT}{x'_1 W} y_{vp} = \frac{(12.61) [2.63 \times 10^{-9}]}{(6.078 \times 10^{-9}) (22.20)} = 0.246$$

$$\text{Theoretical \% U-tube capture} = \frac{0.769 - 0.246}{0.769} \times 100 = 68\%$$

The actual U-tube recoveries, defined as

$$\text{experimental recovery, \%} = \frac{\text{mass DCP in U-tube}}{\text{mass DCP feed stock} - \text{mass DCP raffinate}} \times 100$$

can be calculated from the experimental data to be 62.5% for the three small scale supercritical fluid carbon dioxide extractions of dichlorophenol. This data supports the suggestion that the vapor pressure of the compound being trapped is an extremely critical physical constant when large volumes of CO_2 relative to the aqueous sample volume are being used for the extraction process.

Several experiments were conducted during the program to better define the magnitude of such losses and to design trapping systems which might

TABLE 12. VAPOR PRESSURE OF 2,4-DICHLOROPHENOL*

<u>T, °C</u>	<u>Vapor Pressure, Millimeters Hg</u>
146.0	100
133.5	60
123.4	40
107.7	20
92.8	10
80.0	5
53.0	1
-76.0	2×10^{-6} **

*From Perry, R.H., and C.H. Chilton, eds., Chemical Engineers' Handbook, 5th edition, 1973, p. 13-53.

**Extrapolated from a plot of $\log P$ vs. $1/T$.

mitigate vapor phase loss of the extracted organics. Three alternative approaches for the collection of the organics were identified:

(1) The use of a "U-tube" sequence operated at less than 1 atmosphere and temperatures below -78°C . The use of such a reduced pressure trap would allow lower trap temperatures without collection of solid CO_2 , but would also increase the superficial linear velocity of the gas as it passes through the trap. This type of a system appears feasible, but was not investigated during this program since other concepts seemed to offer comparable or better collection efficiencies.

(2) The use of a collection device containing a solid sorbent such as granular activated charcoal (GAC), Tenax, or an XAD resin to concentrate the organics in the CO_2 effluent stream. Such a system would require subsequent desorption of the organics with the possibility of concomitant contamination and was, therefore, not a major focus of our study. A limited effort, described below, was conducted as part of a test to determine whether vapors of the extracted organics were in fact being lost through the U-tube traps.

(3) The collection of the total CO_2 effluent as a solid or liquid and subsequent isolation of the entrained organic compounds. Such a trapping system would minimize losses of organic substances due to the effects of poor thermal transfer possible in the other trap systems. In addition, if the effluent is collected as liquid CO_2 (e.g., at 900 psi and 20°C), several additional benefits were deemed possible. For example, minimal loss of the organic compounds should occur since their concentration in the gas distilled off is related to their partial pressure above the liquid CO_2 solution. The operation of a trap at 900 psi would also facilitate the use of a recycling system for the CO_2 . Several experiments designed to perform a preliminary evaluation of this type of trapping system are also described below.

A series of experiments were designed to determine whether or not typical model compounds could be recovered when spiked into a stainless steel trap and subjected to a typical supercritical fluid CO_2 extraction procedures. The compounds chosen were 2,4-dichlorophenol, biphenyl 2,2',5,5'-tetra-chlorobiphenyl, caffeine, and anthraquinone. A spiking solution containing these compounds was prepared in acetone at a concentration of 100 $\mu\text{g/mL}$. Calibration standards were also prepared in acetone at 50, 40, 30, and 25 $\mu\text{g/mL}$ concentrations.

As noted, the use of a system which would trap all of the effluent CO_2 as a liquid was of some interest since that approach would limit losses due to poor thermal transfer and entrainment. Subsequent losses to the CO_2 vapor stream would also be minimized when the liquid was slowly boiled off. The five compounds were spiked (50 μg each) into a trapping vessel, and Table 13 shows the recoveries which could be obtained without exposure to any CO_2 .

• Experiment 1

A 0.5 mL aliquot of spiking solution (50 μg each compound/0.5 mL acetone) was added to the trap. The solvent was allowed to volatilize. The trap was attached to the extraction apparatus and liquid CO_2 was pumped into the

TABLE 13. TRAPPING EXPERIMENTS DATA
(μg Analyte)

Compound	Control: Trap Spiked with 50 μg No CO ₂ Treatment (% Recovery)	Experiment 1		Experiment 2		Experiment 3	
		Trap	Spiked with 50 μg (μg Analyte Recovered)	Trap	U-tubes	Trap	U-tubes
2,4-dichlorophenol	65	0		0	0	0	0
Biphenyl	54	0		26	13	7.5	7
2,2',5,5'-Tetrachloro- biphenyl	65	23		26	0	24	0
Caffeine	87	21		19.5	0	22	0
Anthraquinone	100	21.5		22.5	0	26.5	0

trap, and monitored with a sight gauge. (Only a portion of the trap was filled.) The liquid CO₂ was slowly distilled off and trap was then allowed to come to room temperature. Since acetone is a good solvent for each of the compounds under study in this test, the trap and accessible tubing were rinsed with 15 mL acetone and collected in a 25 mL concentrator tube. The concentrator tube was fitted with a micro Snyder column and the acetone concentrated to 1.0 mL.

A 1.0 µL aliquot of extract was injected into a 3% OV-17 6 ft. x 2 mm ID glass column interfaced to a flame ionization detector (FID). The column temperature was programmed from 140°C (isothermal 2 minutes) to 250°C (isothermal 10 minutes) at a rate of 20°C per minute. Calibration standards were also run and recoveries determined. The data are presented in Table 13.

• Experiment 2

As an extension of Experiment 1, a series of 3 U-tubes were attached to the extraction apparatus in order to trap any of the analytes that may have been carried over as the liquid distilled off. Again, the trap was spiked with 50 µg of each compound using the previously described spiking solution. The solvent was allowed to volatilize. The trap was fitted to the extraction apparatus and a series of 3 U-tubes were attached to provide additional trapping of the analytes. The liquid CO₂ was pumped into the trap as described in the previous section with liquid CO₂ being distilled off and passed through the U-tubes. The trap and U-tubes were allowed to come to room temperature. Each was rinsed with acetone and concentrated to 1.0 mL as previously described. These acetone rinses were analyzed by GC/FID along with calibration standards and the results are also presented in Table 13.

• Experiment 3

This was a repeat of Experiment 2; however, a 3% SP 2250 column replaced the 3% OV-17 column.

These results suggest that, even when the organic compounds present in a trap are added as neat materials, the subsequent dilution in liquid CO₂ and distillation processes still result in considerable losses of the subject compounds. Such losses are likely due to chemical reactions, irreversible adsorption or vaporization losses to the CO₂ effluent stream.

A fourth experiment utilizing this trapping system was conducted using higher levels of four selected compounds, and a slightly different sample preparation procedure before analysis.

• Experiment 4

The distillation trap was spiked with 200 µL of acetone containing 400 µg each of 2,4-dichlorophenol, biphenyl, 2,2',5,5'-tetrachlorobiphenyl and caffeine. It was then filled with 400 mL of liquid CO₂. The CO₂ was slowly distilled off and allowed to pass through three glass U-tubes connected in series which were maintained at -76°C. The distillation conditions were as follows:

Bottom and outside of distillation apparatus: 34°C
Inside Apparatus: 22-29°C
Top of Apparatus: 24-27°C
Distillation Rate: 5 standard liters/min.

As part of an effort to develop a more efficient trap rinse procedure, the three U-tube traps obtained in this experiment were rinsed sequentially with CH_2Cl_2 , then CH_2Cl_2 /base (3-5 drops of 6N NH_4OH in 1 mL of CH_2Cl_2).⁴ The results are presented in Table 14.

This experiment demonstrates that sequential washing of the trap system with CH_2Cl_2 and basic CH_2Cl_2 results in higher mass recoveries of the compounds of interest. In order to maximize concentration levels in the rinse solvents for subsequent analysis, such sequential washings had not been conducted in the small scale experiments conducted during this program. Many of the results for trap recoveries may thus represent minimal values. This does not affect the raffinate values, of course.

One experiment utilizing a solid sorbent trap was also conducted to evaluate the concept of vapor losses in the CO_2 effluent stream.

• Experiment 5

An extraction of 400 mL aliquot of water spiked with appropriate salts and the previously noted four model compounds at the one part-per-million level (1 mg/L) was conducted under the following conditions:

Vol. CO_2 : 340 SL
T, °C: 43-46
P, psi: 2400-2600

The extract was collected in three U-tubes connected in series and maintained at -76°C. A sorbent tube packed with XAD-2 resin (500 mg + 250 mg) was attached to the last U-tube. As in the previously described experiment, the U-tubes and raffinate were extracted twice, once with CH_2Cl_2 and once with basic CH_2Cl_2 . The results of experiment 5 are detailed in Table 15. Although this experiment demonstrates the recovery of some of the compounds of concern by the use of solid sorbents on the effluent CO_2 stream, it shows a much more significant recovery from the glass surfaces of the U-tubes utilizing a second solvent rinse. This experiment thus reinforces the above noted suggestion that many of the earlier values presented for recoveries from traps may represent minimal values for recovery. As discussed earlier, the values of analyte in raffinate solutions in all cases were corrected based on extraction efficiencies which were independently determined. They therefore do represent accurately the values of analyte in raffinate solutions.

SMALL SCALE EXTRACTIONS OF INORGANIC SPECIES

Since the presence of high levels of inorganic salts interferes with animal feeding studies, it was also of interest to demonstrate whether or not

TABLE 14. RESULTS OF TRAPPING EXPERIMENT 4

Compound	μg Added	Trap Recoveries (%)								Distillation* Apparatus Residue (%)		
		TRAP 1		TRAP 2		TRAP 3		Total		Wash 1	Wash 2	Total
		Wash	1	Wash	2	Wash	1	Wash	2			
		1	2	1	2	1	2	1	2			
2,4-dichlorophenol*	400	20	-	-	-	-	-	-	-	-	-	-
biphenyl	400	23	5	6	2	2	2	-	-	22	3	25
2,2',5,5'-tetrachlorobiphenyl	400	14	7	-	-	-	-	-	-	40	12	52
caffeine	-	-	-	-	-	-	-	-	-	39	21	60

*A value at the base of the distillation apparatus was not rinsed with CH_2Cl_2 . When the apparatus was dismantled, a phenolic odor was apparent. This observation indicates that the values obtained for Distillation Apparatus Residue are minimal values.

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TABLE 15. TRAPPING EXPERIMENT 5 USING A SOLID SORBENT TUBE

Compound	Trap 1, 2, 3 <u>Recovery</u>	Raffinate Recovery			XAD Recovery		Sum of Compound Recoveries (%)
		Wash		Total	Front	Back	
		1	2				
		(%)					
2,4-Dichlorophenol	33, 0, 0	-	-	-	-	33	
Diphenyl	47, 3, 3	4	5	9	3	65	
2,2',5,5'-Tetra- chlorobiphenyl	27, 8, 4	9	5	14	1	54	
Caffeine	6, 0, 0	48	33	81	4	91	

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AND ILLUSTRATIONS

salts could be carried over and concentrated by this extraction technique. We therefore examined the trapping system after several "blank" runs. In those cases, solutions containing the specified levels of salts (i.e., NaHCO_3 , CaSO_4 , and CaCl_2) as well as PbNO_3 at the 25 ppb level were extracted by supercritical fluid CO_2 . The results for sodium, calcium and lead are shown in Table 16 and indicate that salts of these ions were not collected in the traps.

CHLORINE RESIDUAL EXTRACTION

A 400 ml solution of distilled water containing 70 ppm sodium bicarbonate, 120 ppm calcium sulfate, and 47 ppm calcium chloride was extracted under the conditions detailed in Table 17. Similarly, a solution containing all of those materials plus a 2 ppm chlorine residual (prepared using NaOCl) was extracted as noted. Analysis of the U-tube traps, feedstock and raffinate solutions in each case (blank and chlorine residual samples) showed that no new chlorinated compounds were formed by the presence of a chlorine residual.

TEN LITER EXTRACTION OF TWENTY-THREE ORGANIC SPECIES

At the conclusion of this program, a series of four ten liter extractions were run as follows:

Run #1: 10 liters of distilled, deionized water spiked with 23 organic analytes and specified levels of inorganic salts,

Run #2: 10 liters of distilled, deionized water spiked only with calcium and sodium inorganic salts, and

Run #3 and #4: Replicates of Run #1.

Table 18 describes the sample spiking procedure for Runs 1, 3 and 4.

Based on scale-up considerations from 0.4 liter runs, each sample extraction was conducted at 1950 ± 50 psi and $37-45^\circ\text{C}$, took about 110 minutes, and involved passing approximately 11,200 standard liters of carbon dioxide through the aqueous solution. Since there was a possibility that pressure/flow rate excursions might occur in the large scale apparatus which would lead to the rupture of glass traps, a series of three stainless steel impingers maintained at -76°C were used to collect the organics present in the effluent carbon dioxide stream.

In addition, we have already noted that the small scale extraction experiments had shown that quantitative removal of organics from the traps was a problem for some compounds, perhaps due to the small quantities of collected organics on the large trap surfaces. Therefore, a trap rinse sequence was designed which would assure the dissolution of any of the types of organic compounds which could be recovered from the trap. The solvents used also needed to be compatible with any derivatization/sample preparation steps necessary before analysis. Thus, at the conclusion of each experiment, the three traps were rinsed sequentially with methylene chloride, methylene

TABLE 16. EXTRACTION OF AQUEOUS SALT SOLUTIONS

Analyte	Sodium Analysis* (mg)	Calcium Analysis** (mg)	Lead Analysis*** (ug)
Distilled Water			
Total Traps	0.15	0.03	0.1
Raffinate	<0.02	0.03	<0.4
Solution No. 1			
Total Traps	0.08	0.06	0.4
Raffinate	8.0	15.2	2.0
Solution No. 2			
Total Traps	0.03	0.01	0.1
Raffinate	8.0	16.0	7.2
Solution No. 3			
Total Traps	0.11	0.04	0.2
Raffinate	8.8	16.0	12.0

*Total sodium expected in solutions = 7.7 mg.

**Total calcium expected in solutions = 16.2 mg.

***Total lead expected in solutions = 15.6 ug.

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TABLE 17. EXTRACTION CONDITIONS FOR CHLORINE RESIDUAL STUDY

	<u>"Blank" Run Conditions</u>	<u>"Residual Chlorine" Conditions</u>
Temperature (°C)	40-44	42-50
Pressure (psig)	2400-2600	2400-2600
CO ₂ Volume (S.L.)	200	300

6-1/2"

Sample Preparation

Feedstock and Raffinate: Microextracted
180 mL aliquot + 60g NaCl + 2 mL hexane
Shake 15 min. on wrist-action shaker

U-Tubes: Rinse 3X with 1 mL hexane

Analysis Conditions: GC/ECD
Column: 3% OV-17 on 100/120 Chromosorb WHP
ECD Temperature: 300°C
Injector Temperature: 250°C
Temperature Program: 50°C (3 min) 5°/min → 140°C
(10 min)

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38

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FOR TABLES
AND ILLUSTRATIONS

TABLE 18. SPIKING PROCEDURE FOR RUNS 1,3 AND 4

I. Prepare "SCF" water as follows:

To 10 L Barnsted water add:

700 mg NaHCO_3

1.20 g CaSO_4

470 mg CaCl_2

II. Pump 15 L SCF water into extractor cylinder.

III. Spike the 23 analytes directly into the extractor in the order listed below:

<u>Compound</u>	<u>Volume Spiked/ Spiking Solvent</u>	<u>Total ug Added</u>	<u>Final Concentration</u>
1. 5-Chlorouracil	1.25 mL/4% MeOH- H_2O	500 ug	50 ppb
2. Glucose/Glycine	100 μL /Water	500 ug each	50 ppb each
3. Caffeine/Quinoline/ Anthraquinone	1.0 mL/Acetone	500 ug each	50 ppb each
4. Chloroform/ Phenanthrene	1.0 mL/Acetone	500 ug CHCl_3 10 ug Phenanthrene	50 ppb each 1 ppb
5. Isophorone/Furfural/ Methyl Isobutyl Ketone/Croton- aldehyde	100 μL /Acetone	500 ug each	50 ppb each
6. Biphenyl/2,4- Dichlorobiphenyl/ bis(2-ethylhexyl) phthalate 1-Chlorododecane/ 2,2',5,5'-Tetra- chlorobiphenyl	1.0 mL/Acetone	500 ug Biphenyl, Cl_2 -Biphenyl, BEHP 50 ug C_{12}Cl_1 , Cl_4 -Biphenyl	5 ppb each 50 ppb each
7. Trimesic, Stearic, and Quinaldic Acids	1.0 mL/Acetone	500 ug	50 ppb each
8. 2,4-Dichloro- phenol/BHT	1.0/Acetone	500 ug	50 ppb each
9. Humic Acid	3.25 mL/water, pH=6*	20 mg	2 ppm

IV. Pump remaining water into extractor.

* Humic acid spiking solution prepared as follows: Dissolve 142.47 mg humic acid in 6 mL 0.2N NaOH. Neutralize with 3.7 mL of 0.1M HCl and dilute to 25 mL.

chloride/base (5N NH_4OH added dropwise to each trap), and Milli-Q water. The first methylene chloride trap rinse yielded some aqueous phase extract (approximately twenty milliliters) which was added to the Milli-Q rinse. Aliquots of the trap rinses, raffinate and feedstock, were analyzed according to methods previously developed for the groups of interest. Table 19 summarizes the results obtained from these runs. In general, the types of compounds which were extracted and trapped were the same as those found in the small scale experiments. In particular, the hydrocarbons and phenols were collected in the traps, whereas more polar compounds such as the acids, glucose, and glycine were not detected in the trapping system. The mass balances for some types of materials (e.g., 5-chlorouracil and the humic acid) were poorer in the 10 liter extraction; however, these runs were the first which contained all twenty-three compounds at the same time and the extractions were also conducted for a longer period of time. It is possible that the interactions between compounds under the acidic extraction conditions accounts for the lower total recoveries in certain of these cases. For example, the absence of humic materials in the raffinate and the observation of a brown organic material (humics) upon cleaning the extractor indicate that this material was precipitated out of the solution.

It is of interest to note the total organic carbon analyses (TOC) performed on selected samples identified in Table 20. The high feedstock values are due primarily to the amount of organic solvent added to the spikes as detailed in the earlier table describing the preparation of the 10 liter feedstocks). These results indicate approximately 90% extraction efficiency of organic content from the aqueous feedstock and probably represent good indicators of the overall extraction efficiency of this process for volatile organic species such as acetone.

TABLE 19. SUMMARY OF TEN LITER EXTRACTION

Group	Nominal Spike ($\mu\text{g/L}$)	% Recovered from Traps				% Recovered [†] from Raffinate			
		Run 1		Run 3		Run 1		Run 3	
		Run 1	Run 3	Run 1	Run 3	Run 1	Run 3	Run 1	Run 3
(1)	1-chlorododecane	5	38	21	16	*	*	*	*
	2,2',5,5'-tetrachlorobiphenyl	5	34	35	22	*	*	*	*
	biphenyl	50	30	11	8	*	*	*	*
	bis(2-ethylhexyl)phthalate	50	28	35	26	*	*	*	*
	2,4'-dichlorobiphenyl	50	49	46	40	*	*	*	*
(2)	crotonaldehyde	50	5	3	1	2	2	3	3
	furfural	50	5	4	*	*	*	*	*
	isophorone	50	23	34	27	*	*	*	*
	methylisobutyl ketone	50	4	5	5	4	7	2	2
(3)	anthraquinone	50	24	64	7	29	65	*	*
	quinoline	50	13	*	*	58	35	*	*
	caffeine	50	7	11	*	103	77	34	34
(4)	2,4-dichlorophenol	50	23	36	20	*	*	*	*
	2,6-di-t-butyl-4-methylphenol	50	46	26	20	*	*	*	*
(5)	quinaldic acid	50	*	*	*	83	83	100	100
	trimesic acid	50	*	*	*	98	89	65	65
	stearic acid	50	*	*	*	37	18	26	26
(6)	glucose	50	*	*	*	-	-	-	-
	glycine	50	*	*	*	-	-	-	-
(7)	chloroform	50	NA	NA	NA	*	*	*	*
(8)	phenanthrene	1	18	13	12	*	*	*	*
(9)	5-chlorouracil	50	7	14	7	14	11	13	13
(10)	humic acid	2000	1	1	1	†	†	†	†

* = not detected, refer to Appendix for method detection limits.

NA = not analyzed

† = none detected, brown precipitate was recovered from the extraction upon cleaning. - = insufficient sample was retained to analyze these samples and meet detection limit constraints.

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TABLE 20. TOTAL ORGANIC CARBON CONTENT OF SELECTED TEN LITER RUN SAMPLES

<u>Sample Description</u>	<u>TOC, mg/L</u>
Raffinate, Run #1	22
Raffinate, Run #2	16
Raffinate, Run #3	18
Raffinate, Run #4	15
Feedstock, Sample 1	160
Feedstock, Sample 2	155

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APPENDIX A

SAMPLE PREPARATION AND ANALYSIS PROCEDURES

SAMPLE PREPARATION AND ANALYSIS PROCEDURES

GROUP 1	SAMPLE PREPARATION		ANALYSIS
Compounds	Traps	Raffinate/Feedstock	
2,4-dichloro-biphenyl	<u>Small Scale:</u> Rinse three times with minimal aliquots of diisopropyl ether. Record volume (2-3 mL each trap).	Microextraction: 180 mL aliquot + 60g NaCl into 1 mL diisopropyl ether	GC/FID: Column: 6x2 mm OV-101 on 80/100 port
bis(2-ethylhexyl)-phthalate			Column Temp: 130°/min + 250°C
biphenyl	<u>Ten Liter:</u> Use methylene chloride and methylene chloride/base rinses.		Injector Temp: FID Temp: 235°C
1-chlorodecane			

SAMPLE PREPARATION AND ANALYSIS PROCEDURES

GROUP 2

SAMPLE PREPARATION

ANALYSIS

Compounds

Traps

Raffinate/Feedstock

Small Scale:

Purfural

DNPH* Derivatization

DNPH* Derivatization

HPLC/UV:

Crotonaldehyde

1. Add 90 mL DNPH solution (1 mg/mL DNPH in 2N HCl); let stand.

1. 166 mL aliquot + 200 mg DNPH + 34 mL HCl; let stand overnight.

Column: 30 cm x 3.9 mm (ID) Zorbax ODS, 5 µm particle size

Isophorone

2. Extract with 2x2 mL toluene.

2. Extract with 2 mL toluene.

Mobile Phase: 55/45 CH₃CN-H₂O linear gradient (25 min) to 95/5

47

Methyl isobutyl ketone

3. Wash toluene extract with 2N HCl and distilled deionized water.

3. Sequential rinses toluene extract of 2N HCl and distilled, deionized water.

UV: λ340 nm

4. Evaporate under N₂ at ~ 35°C, dilute to volume with CH₃CN (3 mL or 0.5 mL depending on expected concentration).

4. Evaporation under N₂ at ~ 35°C, dilution to 3 mL with CH₃CN.

Ten Liter:

As above for all trap rinse components.

*2,4-dinitrophenyl hydrazine.

Reference: J. Chromat. Sci., 17:264-268 (1979).

SAMPLE PREPARATION AND ANALYSIS PROCEDURES

GROUP 3	SAMPLE PREPARATION		ANALYSIS
	Compounds	Traps	
	Anthraquinone	Small Scale:	
	Caffeine	1. Add 3 drops 5 N NH ₄ OH; rinse ~ 10 mL CH ₂ Cl ₂ .	GC/FID: Column: 6x2 mmID, 3% OV-17 on 100/120 Chromosorb WHP Column Temp: 140°C (2 min) 40°C/min + 250°C (8 min)
	Quinoline	2. Dry extract through 5 g Na ₂ SO ₄ .	Injector Temp: 225°C
		3. Add 30 ng 2,4- dinitrotoluene as internal standard.	Fid Temp: 275°C
		4. Concentrate to 500 μL using Kuderna- Danish apparatus	

Ten Liter:

Use methylene chloride
and methylene chloride/
base rinses as above.

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SAMPLE PREPARATION AND ANALYSIS PROCEDURES

ANALYSIS

SAMPLE PREPARATION

GROUP 4

Compounds

2,4-dichlorophenol
2,6-di-t-butyl-
4-methylphenol

Traps

Small Scale:

Rinse three times
with minimal aliquots
of diisopropyl ether.
Record volume (~
2-3 mL each trap).

Large Scale:

Use methylene chloride
rinses.

Raffinate/Feedstock

Microextraction:

1. 180 mL aliquot +
60g NaCl into 2
mL diisopropyl ether.

GC/FID:

Column: 1x2 mmID, 1% SP
1240 DA on 100/120 Supel-
coport

Column Temp: 85°C (1 min)
10°/min + 170°C (30 min)

Injector Temp: 190°C

FID Temp: 225°C

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49

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SAMPLE PREPARATION AND ANALYSIS PROCEDURES

SAMPLE PREPARATION

ANALYSIS

GROUP 5

Compounds

Traps

Small Scale:

Raffinate/Feedstock

Stearic acid

Quinaldic acid

Trimesic

Diazomethane
Esterification:

1. Rinse three times with distilled, defonized water. Dilute to 100 mL.

Diazomethane
Esterification:

1. Acidify 100 mL aliquots with HCl.

GC/FID:

Column: 6x2 mm ID, 5% DEGS on 100/120; Supelcoport/3% OV-17 on 100/120 gas chromatograph.

2. Prepare as in raffinate/feedstock.

2. Transfer to column containing XAD-7 resin. Elute with MeOH.

Ten Liter:

Use water rinse and evaporated methylene chloride and methylene chloride/base rinses as above.

3. Evaporate eluant with N₂. Redissolve in 100 µl MeOH.

4. Esterify with 1 mL diazomethane generated in chloroform

Reference: G.A. Junk et al., J. Chromatog., 94:745(1974), and H.M. Fales, T.M. Jaoum and J.F. Babashak, Analytical Chemistry, 45:2302(1973).

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SAMPLE PREPARATION AND ANALYSIS PROCEDURES

ANALYSIS

SAMPLE PREPARATION

GROUP 6

Compounds

Traps

Raffinate/Feedstock

Small Scale:

Glucose

TMS*/Oxime
Derivatization

TMS/Oxime Derivatization

GC/FID:

Glycine

1. Rinse three times with distilled, deionized water. Record volume (~ 50 mL each trap

1. Dry sample using rotary evaporation.

Column: 6x2 mm ID, 3% OV-17 on 100/120 Chromosorb WHP

Column Temp: 120°C (2 min) 20°/min + 250°C (8 min)

Injector Temp: 225°C

FID Temp: 300°C

2. Prepare as in raffinate/feedstock.

2. Dissolve residue in 1.0 mL STOX solution in pyridine and let stand 30 minutes.

Ten Liter:

Use water rinse.

3. Derivatize with TSLM* solution.

4. Solvent exchange extract into 1.0 mL MeCl₂ using N₂.

*N-trimethylsilylimidazole.

Reference: Modification of Method by Brittain, Sullivan, Schewe, "Recent Advances in Gas Chromatography," Domsy and Perry, eds., Marcel Dekker, pp. 223-229 (1971) as described in Pierce Handbook and General Catalog 1979-1980, pp. 182-184 (1978).

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SAMPLE PREPARATION AND ANALYSIS PROCEDURES

ANALYSIS

SAMPLE PREPARATION

GROUP 7

Compounds

Chloroform

Traps

N/A

Raffinate/Feedstock

Microextraction:

1. 100 mL aliquot + 5 mL
iso-octane.

GC/ECD:

Column: 20M x 0.3 mm DB-5
capillary

Column Temp: 45°C (7 min)

Injector Temp: 150°C

ECD Temp: 200°C

Reference:

Adapted from Mreunanen and R. Kroneld, "Determination of Volatile Hydrocarbons in Raw and Drinking Water, Human Serum, and Urine by Electron Capture GC," J. Chrom. Sci., 20:449-454 (October 1982).

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52

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SAMPLE PREPARATION AND ANALYSIS PROCEDURES

SAMPLE PREPARATION

Compounds

Phenanthrene

Traps

Small Scale:

Rinse three times
with minimal ali-
quots of MeOH.
Record volume
(2-3 mL each trap).

Ten Liter:

Use methylene
chloride rinses.

Raffinate/Feedstock

Microextraction:

1. 180 mL aliquot +
60g NaCl + 2 mL
hexane
2. Solvent exchange
extract to 2 mL
MeOH using N₂.

ANALYSIS

HPLC/Fluorescence:

Column: 30 cm x 3.9 mm
ID, PE HC ODS Sil-x,
5 µm

Mobile Phase: 85% MeOH/
15% water, 7 min isocra-
tic

Fluorescence: λEX 280,
λEM 360 nm

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SAMPLE PREPARATION AND ANALYSIS PROCEDURES

ANALYSIS

SAMPLE PREPARATION

GROUP 9

Raffinate/Feedstock

Compounds

Traps

Small Scale:

Rinse three times
with distilled
deionized water.
Record final
volume (10 mL
each trap).

5-Chlorouracil

HPLC/UV:

Column: Lichrosorb RP-2
C8, 5 μ m

Mobile Phase: 10% MeOH/
90% water

UV Detector: λ 280 nm

Direct injection.

Ten Liter:

Use water rinse.

54

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SAMPLE PREPARATION AND ANALYSIS PROCEDURES

ANALYSIS

SAMPLE PREPARATION

Raffinate/Feedstock

Traps

GROUP 10

Compound

Humic Acids

Small Scale:

1. Rinse three times with minimal aliquots of MeOH (12.5 mL each trap)*.

2. Dilute with an equal amount of distilled deionized water to obtain a 50% MeOH/50% H₂O solution.

Large Scale:

Use evaporated methylene chloride and methylene chloride/base rinses and water rinse.

HPLC/UV:

Column: 30 cm x 3.9 mm ID, μ Bondagel E-125, 5 μ m particle size

Mobile Phase: 50% MeOH/50% water, 15 minutes isocratic

*No humic material could be detected visually; although humics were only slightly soluble in MeOH, this rinse was performed to assure the absence of trace humic materials.

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APPENDIX B

TYPICAL SAMPLE PREPARATION AND ANALYTICAL QA/QC DATA

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SUMMARY OF RECOVERY DATA MICROEXTRACTION/DERIVATIZATION TECHNIQUES

Analyte	n	Mean Percent Recovery	Standard Deviation	Coefficient of
				Variation %
2,4'-Dichlorobiphenyl	6	96	18.1	18.8
2,2',5,5'-Tetrachlorobiphenyl	6	87	17.9	20.6
Bis(2-ethylhexyl)phthalate	6	85	22.5	26.5
1-Chlorododecane	3	131	7.8	6
Biphenyl	6	98	11.8	12.0
Fufural	3	61.5	16.5	26.8
Crotonaldehyde	3	83.7	12.0	14.3
Isophorone	3	82.4	10.7	12.9
Methyl Isobutyl Ketone	3	63.1	28.1	44.4
Anthraquinone	3	66.7	19.3	66.7
Quinoline	4	70.8	19.9	28.1
Caffeine	4	86.1	10.6	12.3
2,4-Dichlorophenol	7	86	19.8	23.1
2,6-Di-t-butyl-4-methylphenol	7	76	10.5	13.9
Quinaldic Acid	3	9.1 ¹	0.7	7.7
Trimesic Acid	3	95.8 ¹	3.3	3.4
Stearic Acid	3	78.1 ¹	8.8	11.2
Chloroform	12	80		
Phenanthrene ²	6	69.2	9.7	14.0

¹Recovery from XAD-7 resin.

²M. Reunanen and R. Droneld, "Determination of Volatile Halocarbons in Raw and Drinking Water, Human Serum, and Urine by Electron Capture GC", J. Chrom Sci., Vol. 20, pp 449-454 (October 1982).

LINEAR REGRESSION STATISTICS AND DETECTION LIMITS FOR ANALYTICAL FINISH

Compound	Detection Limit ($\mu\text{g/mL}$)	Calibration Range	n	cc	s	b
2,4'-Dichlorobiphenyl	1.0	1-15 $\mu\text{g/mL}$	10	.9993	245.53	-589.7
2,2',5,5'-Tetrachlorobiphenyl	1.0	1-15	10	.9998	818.38	-101.67
Bis(2-ethylhexyl)phthalate	1.0	1-15	10	.9991	933.38	-159.18
1-Chlorododecane	3.24	2-25	9	.9962	1482	-2284
Biphenyl	3.38	2-25	9	.9959	1892	-2443
Purfural	1.0	1-25 $\mu\text{g/mL}$	5	.9999	175.8	15.54
Protonaldehyde	1.0	1-25	5	.9998	314.0	18.69
Isophorone	1.0	1-25	5	.9999	171.3	13.52
Methyl Isobutyl Ketone	1.0	1-25	5	.9999	237.1	24.83
Anthraquinone	13.0	13-110 $\mu\text{g/mL}$	8	.9992	.037	.038
Quinoline	20.0	20-160 $\mu\text{g/mL}$	8	.9998	.024	-.018
Caffeine	15.0	15-120 $\mu\text{g/mL}$	8	.9982	.012	-.010
2,4-Dichlorophenol	5.0	5-15 $\mu\text{g/mL}$	8	.9975	2079.64	-531.84
2,6-Di-t-butyl-4-methylphenol	2.5	2.5-15 $\mu\text{g/mL}$	11	.9987	5049.19	-1527.28
Quinaldic Acid	.01	.01-.05 $\mu\text{g/mL}$	4	.9991	1794	655.0
Trimelic Acid	.01	.01-.05	4	.9992	1569	-210.0
Stearic Acid	.01	.01-.05	4	.9994	1202	-580.0
Glucose	252	25-40 $\mu\text{g/mL}$	4	.9920	1.3x10 ⁵	-6.5x10 ⁵
Glycine	302	30-50 $\mu\text{g/mL}$	3	.9820	.150	-2.667
Chloroform	.14	.01-.375 $\mu\text{g/mL}$	6	.9689	.188387	.121985
Phenanthrene	.023	.01-.08 $\mu\text{g/mL}$	5	.9966	6428.48	21149
5-Chlorouracil	.014	.01-.05 $\mu\text{g/mL}$	11	.983	75458.61	216.91
Humic Acid	.68	.02-4.0 $\mu\text{g/mL}$	5	.9980	16.51	2.77

¹ Calculated for the 95% Confidence Limit using Hubaux, A. and G. Vos, "Decision and Detection Limits for Linear Calibration Curves," Anal. Chem. Vol. 42, No. 8, pp. 849-855 (July 1970).

² Includes recovery from derivatization technique. Does not use Hubaux and Vos calculation